Purification and surface modification of Carbon nanocapsules synthesized by electric plasma discharge in the ultrasonic cavitations field(超音波アークプラズマ法により作成した磁性金属内包カーボンナノカプセルの精製と表面改質)

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論文内容要旨

The extraordinary properties of carbon nanocapsules (CNCs) make efforts to develop simple and inexpensive method for large-scale production of these materials. This study demonstrates the newly developed process that can be categorized as a new wet process to synthesize carbon nanocapsules utilizing an electric plasma discharge in ultrasonically irradiated organic liquids. The ultrasonic cavitation field consisting of thousands of tiny activated bubbles triggers off the plasma discharge in insulating organic liquids such as benzene, hexane and ethanol using relatively low capacity of electric power supply. Figure 1 shows a schematic diagram of the experimental apparatus. An ultrasonic homogenizer with a titanium horn was used in the experiments to irradiate 100 ml of organic liquids at 600 W and 20 kHz. Argon gas flow was directed into a glass vessel to maintain an inert atmosphere. During the ultrasonic irradiation, the voltage on the electrodes was kept at 55 V using a constant voltage power unit and the upper limit of the current on the electrodes was set about 1.58-3 A throughout the experiment. As shown in Fig. 1, two metal electrodes (2 mm) are inserted 1 mm apart from each other just beneath but very close to the bottom of the ultrasonic horn. Thus, the plasma discharge in organic liquids occurred at electric supply powers as low as 87-165 W.

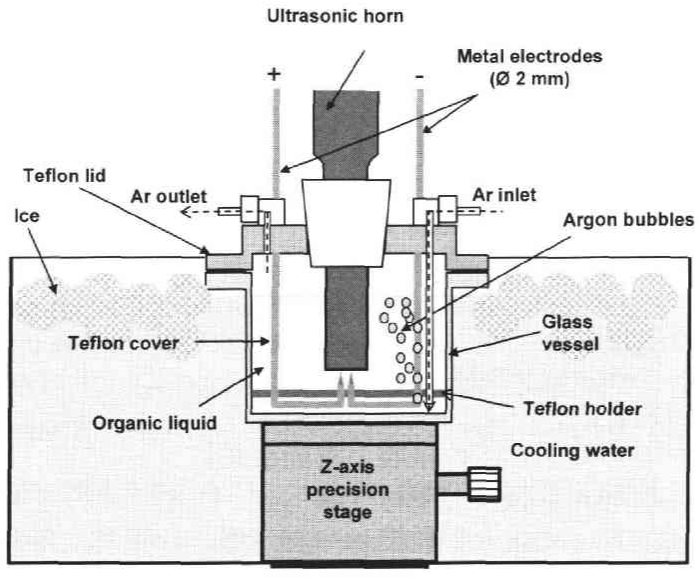


Figure 1 Schematic diagram of the experimental apparatus.

By selecting the materials for the ultrasonic tip and the electrodes, investigators may find it possible to use this new method for continuous production of magnetic metal or metal carbide nanoparticles encapsulated by graphite shells.

Synthesis of iron filled carbon nanocapsules by an electric plasma in an ultrasonic cavitation field in liquid ethanol.

Magnetic nanoparticles of pure metals such as Fe, Co, Ni are used as materials in various field of magnetism. The main difficulty for the use of pure metals arises from their instability towards oxidation in air, which become easier as the size gets smaller. One approach to chemical stabilization is the formation of protective shells on the nanoparticles surface that prevent the reaction of oxygen with the surface atoms. Carbon coating is effective protection against environmental degradation and has excellent adhesive bond with surface of metal particles. In the past research we concentrated on the structure, magnetic properties and synthesis method of metal nanoparticles encapsulated in graphite shells, in other words, carbon nanocapsules (CNCs). Unique combination of ferromagnetic core and protective carbon (graphite) shell(FIG. 2) can find various practical applications in such as the biomedicine, the magnetic recording industry, the field of ferrofluids, etc. One of the prospective medical applications of magnetic CNCs can be the drug delivery to the specified targets. Drug molecules and targeting ligands molecules can be covalently attached to the graphite carbon shell via carboxyl groups and then injected intravenously and directed using the external magnetic field, through the blood vessel system, to the region of interest for treatment.

Thus, the **purpose** of the past research was synthesis of CNCs by a newly developed method and analysis of the structure and magnetic properties of the CNCs. The **objects** of investigation in past work were two types of metal materials (Fe, Co) encapsulated in graphite shells.

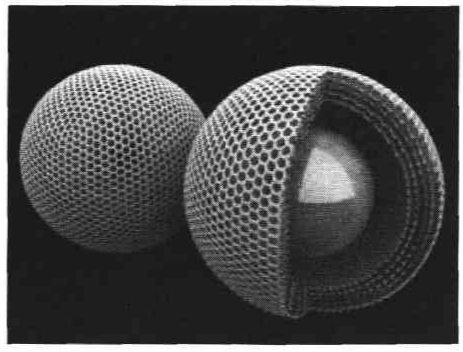


Fig.2 Computer image of carbon nanocapsule

Newly developed sample purification and separation

One of the conventional and efficient techniques for removal of amorphous carbons is the thermal or plasma cleaning with Ox (x≈2), and another is treatment with a toxic gas such as halogen. However, these techniques slightly attack the graphite shell as well as amorphous carbon, and may also require the disposal of hazardous substances. In this study, to remove the amorphous carbons we have conducted the selective-oxidation method using hydrogen peroxide, which is one of the safety and conventional methods. After this stage purification, we have arrived at two different problems. One is graphite flakes or balls which were not oxidized by hydrogen peroxide. Another problem is the wide size-distribution of purified carbon nanocapsules from 30 to 1000 nm. Hydrogen peroxide has removed the small-size carbon nanocapsules (less than 20 nm in diameter). The purpose was to separate the CNCs of about 100 nm in diameter because this size of carbon nanocapsules can be used for the drug delivery system (DDS). This problem was solved by centrifugation method. Sharp size distribution can be gained using the centrifugation at a speed of rotation around 4000 rpm (See FIG. 3.).

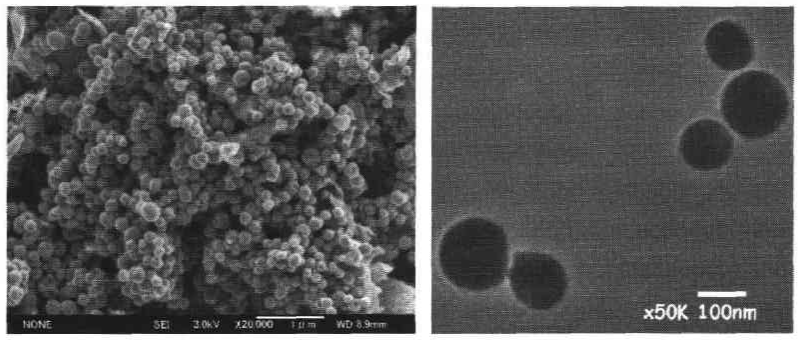


Fig. 3 SEM and TEM images of purified and separated carbon nanocapsules.

So, for production of nanoparticles for the DDS we must purify the synthesized powder as much as possible from the unwanted carbon (amorphous carbon, graphite balls) and metal impurities and get the desired size distribution. And then the purified and separated particles can be covered with biocompatible polymer coatings. At present time we successfully solved the problem of removal of the exposed metal particles, amorphous carbon and getting of the sharp particle distribution by the etching in a 15 % HCl, the selective-oxidation method using hydrogen peroxide and the centrifugation, respectively. Monodispersed, low-dimension iron particles covered by graphite layers are foreseen to exhibit outstanding properties, which could find applications in the drug delivery. We found a moderate centrifuge speed (4000 rpm) which has particle size distribution of 100~200 nm. In future, we will develop the magnetic drug carrier of carbon nanocapsules, which are functionalized by

biocompatible polymer and target ligand. The schematic figure of the research concept is shown in Fig. 4.

Our task should be further purification of synthesized powder from graphite flakes and balls and surface coating of the carbon nanocapsules by a thin film of biocompatible materials to get specific physical, chemical, and biomedical properties. Conventional nanoparticle coating methods include dry and wet approaches. Dry methods include the follows: physical vapor deposition, plasma treatment, chemical vapor deposition, and pyrolysis of polymeric or non-polymeric organic materials for in-situ precipitation of nanoparticles within a matrix. Wet methods for coating nanoparticles include sol–gel processes, emulsification and solvent evaporation techniques. Among different methods we selected the easiest emulsification and solvent evaporation techniques, which continue to the further attachment of target ligand on the surface.

(1) The graphite flakes and balls can be easily removed by magnetic separation. The magnetic separator design includes the application and travel of a permanent magnet to the wall of a test tube to cause aggregation. As-prepared sample wsa dispersed in test tube with ethanol solvent and then tube is moved by a precise motorized stage along the strong permanent magnets.

(2) Coating of carbon nanocapsules with the biocompatible polymers

Magnetic nanoparticles offer some attractive possibilities in biomedicine. The attempt which uses the magnetic nanoparticles in the drug delivery system (DDS) as the magnetic carrier is done actively by many researcher, also these pasticles can be use as MRI(Magnetic Resonance Imaging) contrast agent. Magnetic nanoparticles have controllable sizes ranging from a few nanometers up to tens of nanometers, which places them at dimensions that are smaller than or comparable to those of a cell (10–100 μm), a virus (20–450 nm), a protein (5–50 nm) or a gene (2 nm wide and 10–100 nm long). The magnetic nanoparticles and the high-molecular polymers are one of the problematical points for connection to be weak. As for the carbon nanocapsules filled with the magnetic metals (Fe, Co), their graphite shells have a good affinity with high-molecular polymers. The magnetic particles are usually coated by a biocompatible polymer such as PVA, dextran or PEG and inorganic coatings such as silica which have been recently developed. The biocompatible coating acts to shield the magnetic particle from the surrounding environment and can also be functionalized by attaching carboxyl groups, biotin, avidin, carbodi-imide and other molecules. **Our achievement** is coating with PEG (polyethylene glycol) on the graphite shell directly (Fig 5) because PEG is non-toxic and is used in a variety of products such as block copolymer which prevents to stick to protein, a number of toothpastes as a dispersant and it is the basis of many skin creams. The coating procedure are applied continuously to attach the target ligand on the surface of the polymer.

(4) Evaluation of the property of the magnetic carrier of carbon nanocapsules

The magnetic properties of polymer coated carbon nanocapsules are measured by VSM. The coated polymer of the carbon nanocapsule, i.e. its coating thickness, uniformity and adhesion will be observed with scanning and transparent electron microscopy (SEM and TEM). In addition, chemical form of the surface coated by polymer and functionalized by target ligand will be investigated with TG-DTA, FT-IR and Raman spectroscopy.

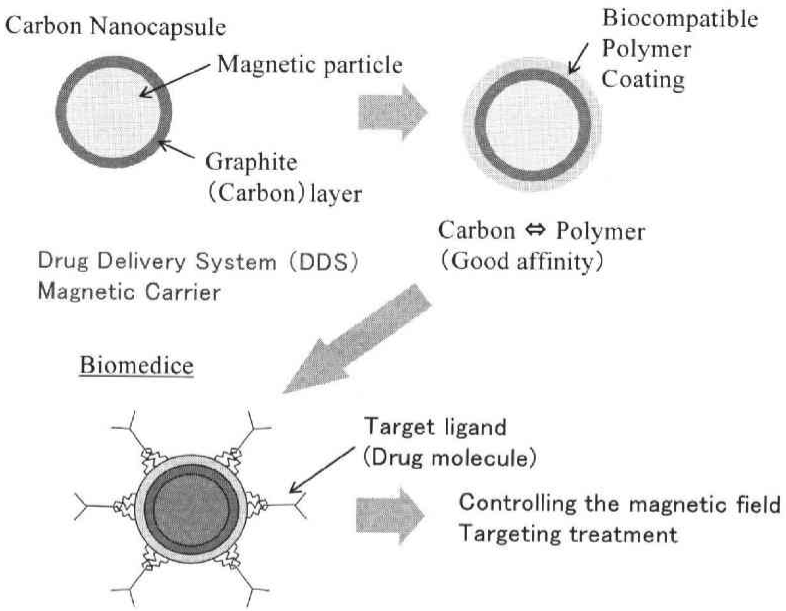
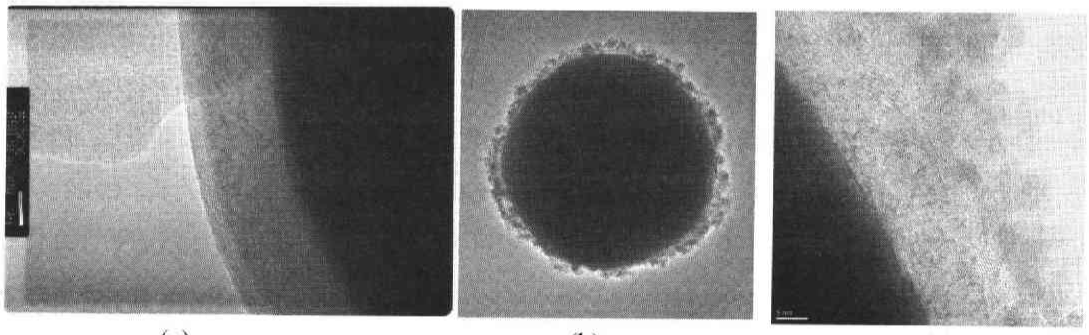


Fig. 4 Schematic diagram of the research concept of development of DDS magnetic carries of carbon nanocapsules



(a) (b) (c)

Fig. 5 PEG coated on carbon nanocapsules

論文審査結果の要旨

第1章は緒論であり、金属内包ナノカプセルの合成法、応用についてこれまでのレビューを行い、この研究の学術的意義の十分な把握を行った。特に本論文は、従来使用されていない超音波アーク放電法による磁性材料のナノカプセル合成で、あり、同時に副製するアモルファスカーボンやカーボン片の生成状態が従来のものと大きく異なるので、精製法についても新たな検討が必要であることを明らかにした。

第2章では、具体的に超音波アーク放電法による炭化鉄内包ナノカプセル合成で生成する不純物の除去に関して研究を行った。アモルファスカーボンを代表とするその他のカーボン系不純物を空気やCO2などで酸化除去するのは効率が悪いことがわかった。最終的にアモルファスカーボンは常温の過酸化水素水、カプセル化されていない金属ナノ粒子や炭化物ナノ粒子は塩酸で溶解除去可能で、さらに磁気分離や遠心分離の手法を用い、サブミクロンから数十ナノのサイズに分類できることを明らかにした。

第3章では、粒度を目的の100−200nmに調整した炭化鉄内包カーボンナノカプセル表面上に生体適応性の高いPEGを修飾することを目指して検討を行った。従来適応されている水溶液中に溶解し、析出させる方法では、不均一にPEGが修飾され、問題があることがわかったので、新たに有基溶媒を用いたゾルーゲル法を開発し、カーボンナノカプセルにPEGを全面的にコーティングできることを見出した。これにより、このナノカプセルをDrug Delivery System(DDS)の粒子として使用できる可能性を明らかにした。

第4章では、炭化鉄では磁性が弱いので、さらに高磁性のカーボンナノカプセルを合成するために、Pt-Fe系の磁性材料をナノカプセル化することを目指し、従来用いてきた電極を鉄からPt-Fe合金に変更し、Pt-Fe合金内包カーボンナノカプセルの合成を試みた。その結果、生成するPt-Fe合金内包カーボンナノカプセルの粒度範囲が炭化鉄の場合より広く、かち数百nm以上の大きいものではPtリッチのPt-Fe合金、数十nmと小さいものでは、鉄リッチのPt-Fe合金ナノカプセルの割合が多いことがわかった。実際にPtリッチのPt-Fe合金ナノカプセル粒子の磁性測定を行った結果、目的のPt-Fe合金に制御することは難しく、磁性そのものの大きな向上は見られなかった。しかしながら、保持力はかなり向上することが明らかになった。

第5章は結論であり、上記各章を総括している。

以上、要するに本論文は、磁性を持つ金属ナノカプセルの合成法とその精製ならびにPEG修飾法の新プロセスを開発し、超音波アーク放電法による磁性材料のナノカプセルがDDSに適用できることを示したもので、材料工学の発展に寄与するところが非常に多い。よって、本論文は博士（学術）の学位論文として合格と認める。